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MEMORANDUM #8

THERMOELECTRIC PROPERTIES OF
SILICON-GERMANIUM ALLOYS
AS A FUNCTION OF
TIME AND TEMPERATURE

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INTRODUCTION

Recent emphasis on the development of practical high performance thermoelectric power conversion systems capable of reliable long-term operation has brought silicon-germanium alloys and their associated technology into renewed focus. It is generally accepted that of all possible thermoelectric power conversion systems, it is those using silicon-germanium alloys that best combine the desirable qualities of high performance, good reliability and low weight when operated at hot side temperatures of the order of 1700 to 2000°F. Whereas limitations due to maximum heat source operating temperature capabilities have in the past restricted the operation of practical thermoelectric power conversion systems to somewhat lower temperatures, recent developments in high temperature heat source technology have alleviated this situation; as a result, active development work has started on high temperature silicon-germanium thermoelectric systems.

The accelerated emphasis on the practical utilization of silicon-germanium alloys in practical thermoelectric power conversion devices has necessitated a re-examination of the state of the technology. Most gaps still extant in the technology are as a result actively being filled or probably will be filled in the foreseeable future. Even before this is accomplished, however, there exists in some instances a need for interim information required in analytical and design efforts in the definition of a variety of power conversion systems. One area in which the need for such interim information exists is the one of long-term time and temperature dependence of silicon-germanium alloy thermoelectric properties. Although this need really applies to all silicon-germanium alloys, a special requirement, as discussed in greater detail below, has arisen for such material property information for the 80 at/o Si - 20 at/o Ge alloy. It is the purpose of the present memorandum therefore to fill this requirement by presenting analytically derived thermoelectric property data as a function of time and temperature for the phosphorus doped n-type 80 at/o Si - 20 at/o Ge alloy; the corresponding data for the p-type alloy are essentially independent of time and are available in the literature. Nevertheless, for completeness, a set of such data for the boron doped p-type alloy have been re-

produced here. Inasmuch as past uses of silicon-germanium alloys have concentrated on the 63 a/o Si - 37 a/o Ge alloy because of a close match of its expansion coefficient to that of tungsten, a widely used electrode in silicon-germanium thermocouples, and because it is anticipated that this alloy will continue to be used in many future thermoelectric applications, the present memorandum also presents analytically derived thermoelectric property data as a function of time and temperature for the phosphorus doped n-type 63 a/o Si - 37 a/o Ge alloy. For completeness, a corresponding set of data for the boron doped p-type alloy are given also for this alloy.

BACKGROUND DISCUSSION

The design of thermoelectric power conversion systems generally concerns itself with the performance of the system at the end of life because usually, especially in space applications, there exists a minimum performance requirement that the system must satisfy at that time. In designing for the end of life performance, it is necessary to have available information on the time and temperature behavior of various system components individually and in combination in order that a meaningful design may be formulated. Of all the components making up a thermoelectric power conversion system, obviously it is the thermoelectric material and its behavior that usually has the most important bearing on system performance. For this reason, detailed information on the time and temperature behavior of the thermoelectric properties of the active material used in a thermoelectric device is a necessary prerequisite to the practical design of such a device. Knowledge of the characteristics and behavior of other system components is of course also important, especially as concerns the thermal insulation and the extraneous electrical resistance of the circuit, including the hot and cold side contacts between the active thermoelectric material and the current carrying electrodes. Nevertheless, it is information on the thermoelectric properties of the thermocouple leg materials that probably forms the single most important basic piece of information needed in the design of thermoelectric power conversion systems.

A number of thermoelectric materials have been used in the practical conversion of heat to electricity in the recent past, including various lead and tellurium compounds and alloys and silicon-germanium alloys. Inasmuch as most applications to date have required system life-times of one or two years or less, the study, development and test efforts on thermoelectric materials and devices have been mostly limited to actual and/or projected operating times of that order. It is only relatively recently that work has been undertaken to develop thermoelectric systems for applications, primarily in long-term deep space missions, that possess significantly longer life-times. The so-called Grand

Tour of the outer planets now in the planning stages by NASA has a mission time in excess of ten years and exemplifies the recent trend in applications requiring long-term thermoelectric power production. In view of established reliability and attractive performance characteristics in long-term operation, it is primarily thermoelectric generators that use silicon-germanium alloys and associated technology that have come to be considered for applications requiring very long operating times.

Although extensive information exists on the operation of certain silicon-germanium alloys in various thermoelectric modules and devices for extended time periods, in some instances exceeding five years of continuous operation, the information is such that, although it demonstrates the overall reliability and the relatively high performance level obtained with devices of this type, it does not yield detailed thermoelectric property data on silicon-germanium alloys. Such data, needed in the design and the performance analysis of thermoelectric devices, have traditionally been obtained from thermoelectric material studies. Several such studies have been conducted since 1961, the time when silicon-germanium alloys were first suggested in this country as promising thermoelectric materials. Unfortunately, however, most studies concerned with the thermoelectric properties of silicon-germanium alloys have mainly involved the establishment of these properties in the "as-grown" state of the material as a function of alloy composition. Although initial thermoelectric properties are important in material optimization studies and the establishment of initial generator performance characteristics, they do not enable the end-of-life design of a thermoelectric generator because thermoelectric properties frequently change with time. Thus, the thermoelectric properties of silicon-germanium alloys, especially those of the n-type alloys, are well known to undergo changes with operating time as a result of dopant precipitation. Some effort has been devoted to the study of the time dependence of the thermoelectric properties of certain silicon-germanium alloys as a part of the just mentioned material studies. Most of this work has, however, only involved alloys with a

composition of 63 a/o Si - 37 a/o Ge and operating times up to 1500 hours. No experimentally determined thermoelectric material property data thus exist for any silicon-germanium alloys for operating times beyond 1500 hours; for most alloys even these data are not available.

The bulk of the past design effort on silicon-germanium thermoelectric generators has involved generator design life-times rarely exceeding one or two years and the use of silicon-germanium alloys with an alloy composition of 63 a/o Si - 37 a/o Ge. As just discussed, no experimentally determined thermoelectric property data exist for this or any other silicon-germanium alloy for operating times exceeding 1500 hours. It has been the practice therefore to project the thermoelectric properties to any desired operating time by means of analytical techniques. It has been possible to do this reasonably accurately for relatively short operating times, of the order of a year or two, because the mechanism of thermoelectric property change in silicon-germanium alloys is qualitatively well understood. Although projections for longer operating times have also been analytically made, it is not generally known how good such projections are for lack of accurate device performance data at operating times exceeding a few years.

Practically all projected long-term thermoelectric property data on silicon-germanium alloys has involved the alloy with a composition of 63 a/o Si - 37 a/o Ge. Of all silicon-germanium alloys, it is this alloy that up to the present has received by far the most extensive use in practical thermoelectric energy conversion devices because of the compatibility of its thermal expansion characteristics with those of tungsten. Tungsten is commonly used as an electrode material for silicon-germanium alloys. While it has been known for years that of all silicon-germanium alloys, it is alloys with a composition of some 80 a/o Si - 20 a/o Ge that possess the most optimum performance characteristics (maximum figure-of-merit), it has been a question of electrode compatibility that has precluded the practical use of these alloys. In the past there

has not existed much impetus to develop bonding techniques for the higher silicon content silicon-germanium alloy because the performance gains in increasing the silicon content of the alloy from 63 a/o to 80 a/o, although distinct, are not especially great. Recently, however, active efforts have been initiated on an AEC technology program^{*} towards the optimization of all phases of silicon-germanium alloy technology. As a part of this optimization, attention has again been focused on the practical utilization of the 80 a/o Si - 20 a/o Ge alloy.

For completeness, it should be mentioned that in addition to possessing a higher figure-of-merit, the 80 a/o silicon content silicon-germanium alloy also possesses some other advantages over the commonly used 63 a/o Si - 37 a/o Ge alloy. Some of the more important of these are an approximately 100°C higher solidus temperature, a closer match between the thermoelectric properties of the n- and p- type alloys and a slightly higher tensile strength. The higher solidus temperature means that the 80 a/o silicon content silicon-germanium alloy can be operated at temperatures higher than those considered maximum for the 63 a/o Si content alloy. The more closely matched thermoelectric properties of the 80 a/o silicon content n- and p-type silicon- germanium alloys result in nearly equal-sized thermoelements for optimum thermocouple performance. For reasons of symmetry, equal sized thermoelements generally enable the construction of fairly rugged thermocouples. The 63 a/o silicon content silicon-germanium alloy requires n- and p-type thermoelement cross-sectional areas in the ratio of about 1.5 to 2.0 for optimum thermocouple performance. Some ruggedness is lost in this configuration. Finally, indications exist that the thermoelectric properties of the 80 a/o silicon content silicon-germanium alloy generally change less as a function of operating time than those of the 63 a/o silicon content alloy. This means that the performance of devices using the former alloy is more stable than of those that use the latter alloy.

In view of the renewed interest in the utilization of high silicon content silicon-germanium alloys in practical thermoelectric energy conversion

* Contract No. AT (29-2)-2510, RCA, Harrison, New Jersey

devices, the requirement has arisen for thermoelectric property data as a function of operation time for device design purposes. As mentioned, special interest exists in property data for very long-term operation because it is in applications of this type that silicon-germanium alloys are found to be especially attractive. As also mentioned, such data, either experimental or analytical, do not presently exist. It is the purpose of the present memorandum, therefore, to fill this void by presenting analytically derived thermoelectric property data for the 80 a/o Si - 20 a/o Ge alloy as a function of operating time for extended time periods. For completeness, and because it is recognized that silicon-germanium alloys with a silicon content of 63 a/o will continue to be used in many applications, the present memorandum also presents corresponding thermoelectric property data for the 63 a/o Si - 37 a/o Ge alloy.

It is recognized that analytically derived data are no better than the model on which they are based. Although a good qualitative understanding exists of the solid state model underlying the thermoelectric properties of silicon-germanium alloys and the dependence of these properties on time and temperature, considerable effort will still be necessary to formulate a complete quantitative understanding. The only way in which this is possible is through extensive experimental work. In the meantime, however, the analytically derived thermoelectric property data for silicon-germanium alloys presented in this memorandum will temporarily fill a much needed requirement.

PRECIPITATION KINETICS

A fairly good qualitative understanding exists of the time and temperature dependence of the thermoelectric properties of silicon-germanium alloys. Inasmuch as much of this subject has already been covered in fair detail elsewhere*, there exists little reason for the repetition of a detailed discussion here. Nevertheless, in view of its applicability to the topic at hand and for purposes of completeness, a brief summary of the factors underlying the time dependence of the thermoelectric properties of silicon-germanium alloys is appropriate.

The worth of a material for thermoelectric energy conversion is approximately indicated by the so-called figure-of-merit which combines the three thermoelectric properties, the Seebeck coefficient S , the electrical resistivity ρ and the thermal conductivity k in the well known relationship

$$Z = \frac{S^2}{\rho k} . \quad (1)$$

It has generally been established that extrinsic semiconductors with carrier concentration values in the range 10^{19} to 10^{21} carriers per cubic centimeter possess values of figure-of-merit higher than those of any other grouping of materials; silicon-germanium alloys are semiconductors for which the figure-of-merit maximizes in the extrinsic range for carrier concentration values of the order of 2×10^{20} carriers per cubic centimeter. As with extrinsic semiconductors in general, the bulk of the indicated carrier concentration in silicon-germanium alloys is obtained through addition of impurities during crystal growth. Each impurity atom, or dopant atom as they frequently are called, in solid solution in the crystal donates one or more carriers to the lattice. Because of the high carrier concentration required for maximizing the figure-of-merit it is usually found that only a relatively few dopants exist for any given semiconductor that have solid solubilities sufficiently great

* See for example References 1 to 3.

for yielding the desired impurity carrier concentration. In silicon-germanium alloys only certain of the Group III and Group V elements satisfy this requirement.

The addition of Group III elements to silicon-germanium alloys yields material with p-type characteristics because Group III elements possess three valence electrons, one less than is required to form complete bonds with the four nearest-neighbor silicon and germanium atoms. The deficiency of an electron manifests itself exactly as if an electron were neutralized by a positive carrier; hence, the p-type behavior of the crystal. Of all Group III elements, it is boron that has the highest solid solubility in silicon-germanium alloys. In fact, the solid solubility of boron in silicon-germanium alloys is sufficient to enable doping of the alloys to carrier concentration values of the order of 10^{21} carriers per cubic centimeter, far in excess of those required for maximizing the figure-of-merit. Silicon-germanium alloys doped with boron for maximum figure-of-merit are therefore doped considerable below the solid solubility limit of boron in these alloys. The result is that the system of dopant and lattice is in equilibrium and the properties of boron doped p-type silicon-germanium alloys are stable with time and temperature. Although other Group III elements could also be used as dopants, it is boron that because of its high solid solubility is usually used as the p-type dopant for silicon-germanium alloys. The solid solubilities of other Group III elements in silicon-germanium alloys, although relatively great, are smaller than that of boron, and, in fact, in most cases are marginal for the attainment of maximum figure-of-merit values.

The addition of Group V elements to silicon-germanium alloys yields material with n-type characteristics. Group V elements possess five valence electrons, one more than is needed to form complete bonds with the four nearest neighbor silicon and germanium atoms. The excess electron is consequently very weakly bound to its parent atom and thermal energy, even at room temperature is sufficient to unbind it and make it a free carrier. Each Group V dopant atom therefore contributes one n-type carrier to silicon-germanium alloys. In order to obtain a carrier concentration of the order of 2×10^{20} carriers per cubic

centimeter required for maximizing the figure-of-merit of silicon-germanium alloys, it is consequently necessary to dope the alloys to impurity concentrations of the same order. Unfortunately, none of the Group 'V' elements possesses a solid solubility in silicon-germanium alloys sufficient at all temperatures for accomplishing this. Because it comes closest, however, to satisfying the solid solubility requirement, it is phosphorus that is commonly used as the n-type dopant in silicon-germanium alloys.

Phosphorus exhibits a so-called retrograde solid solubility in silicon-germanium alloys. The solid solubility attains a maximum at temperatures of the order of 900 to 1100°C and decreases at both higher and lower temperatures. In order to maximize the figure-of-merit of phosphorus doped silicon-germanium alloys, it is therefore necessary to dope the alloys to impurity concentration values consistent with the maximum solid solubility of dopant at temperatures in the range of 900 to 1100°C. When this is done, however, there exists an excess of dopant at both higher and lower temperatures; silicon-germanium alloys doped in this manner are super-saturated with dopant. Because of the resultant instability, the system of dopant and lattice tends to equilibrium by precipitating any dopant in excess of its solid solubility at any given temperature. This effect of a decreasing dopant, and hence carrier concentration, manifests itself in changed electrical properties as a function of time; both the electrical resistivity and Seebeck coefficient increase with time in such a manner that the quantity S^2/ρ slightly decreases. Inasmuch as the thermal conductivity remains nearly unchanged, the figure-of-merit of n-type silicon-germanium alloys slightly decreases with time.

The rate and extent to which the thermoelectric properties of n-type silicon-germanium alloys change with time is obviously temperature dependent. At the temperatures of maximum solid solubility of phosphorus, the material is in equilibrium and thus little change takes place. At temperatures exceeding those of maximum dopant solid solubility, the precipitation process goes to completion extremely fast because of the high temperatures in question. It is at temperatures

below those of maximum dopant solid solubility that observable long-term changes in the electrical properties of n-type silicon-germanium alloys occur. Because the solid solubility of phosphorus decreases with temperature at temperatures below the solid solubility maximum, the "driving force" for precipitation increases with decreasing temperatures. The diffusion rate of phosphorus in the silicon-germanium matrix, diffusion preceding precipitation at a nucleation site, however decreases with decreasing temperatures. The net result of the opposing temperature dependences of these two mechanisms is that it is at intermediate temperatures in the range of 300 to 700°C that the biggest changes occur in the electrical properties of n-type silicon-germanium alloys as a result of dopant precipitation. At very low temperatures, such as room temperature, precipitation proceeds so slowly as to be practically unobservable.

Although no all-encompassing model exists for quantitatively describing the precipitation of phosphorus in silicon-germanium alloys for all times, Ekstrom and Dismukes⁴ have suggested that a model due to Slyozov and Lifshitz⁵ reasonably accounts for at least a part of the process. In this model the precipitate phase consists of particles of nearly continuously varying radii. The surface energy of the particle-solution interface determines this critical radius. Particles having radii smaller than the critical value tend to redissolve in the matrix whereas particles with radii exceeding the critical radius tend to grow as the precipitation proceeds. The two competing processes initially decrease the precipitation rate to values less than expected from a diffusion limited precipitation process by itself. At long times, after complete dissolution of the small particles, the precipitation rate in silicon-germanium alloys approaches that solely due to a diffusion limited precipitation process. The initial distribution of precipitated particles with nearly continuously varying radii is introduced into the alloys during crystal growth and related high temperature treatments. It should be noted that in materials that exhibit a retrograde dopant solid solubility, nearly invariably there coexist a precipitate phase and a solute phase, even when the overall doping level is purposely kept below the maximum dopant solid solubility level.

According to the model of Slyozov and Lifshitz⁵, a diffusion-limited precipitation process which accounts for the re-resolution of small precipitate particles due to surface energy may be represented by

$$\left[\frac{C_i - C_e}{C_t - C_e} \right]^3 = \left[\frac{1}{9} \left(\frac{C_e}{C_p} \right) \left(\frac{C_i - C_e}{C_e} \right)^3 \frac{D}{\beta^2} \right] t + B, \quad (2)$$

where B is a constant and β is defined as

$$\beta = \frac{2M\sigma}{\delta RT} \quad (3)$$

In the above equations, C_i is the initial solute concentration, C_t is the solute concentration at time t, C_p is the concentration of solute in the precipitate phase and C_e is the equilibrium dopant solid solubility. D is dopant diffusion coefficient at temperature T, M is the mean atomic weight of the matrix, σ is the interphase surface energy, δ is the density of the matrix, R is the gas constant and t represents time. It may appear that the constant B in Eq. (2) should assume the value of unity. Ekstrom and Dismukes⁴, however, point out that B=1 is not physically meaningful if the characteristic precipitate particle size distribution is not present at the start of the precipitation process. The model represented by Eqs. (2) and (3) reasonably accounts for the precipitation of phosphorus in silicon-germanium alloys after the first few hours of the precipitation process. The processes extant during the first few hours appear to be closely related to the previous thermal history of the alloys; it is not uncommon for the carrier concentration to remain constant or even increase initially. Although Ekstrom and Dismukes⁴, obtained good agreement between theory and experiment for precipitation times exceeding a few hours, most of their work involved only the first 1000 hours of the precipitation process. It is therefore not precisely known how good the agreement between theory and experiment is at much longer precipitation times. An approximate indication of the validity of the theory at longer times, however, has been obtained by attempts to apply it to thermoelectric property data derived from device characteristics in long-term

operation. Although device data have thus indicated some validity of the theory at longer operating times, it must be remembered, as already discussed above, that thermoelectric property data derived from device performance are typically quite imprecise; at best, therefore, a comparison of this type can only point out gross discrepancies between theory and experiment. On the other hand, although not fully established, there is no special reason at this time to not believe in the applicability of the theory and thus not make use of it in predicting the long-term behavior of the thermoelectric properties of silicon-germanium alloys.

THERMOELECTRIC PROPERTIES OF SILICON-GERMANIUM ALLOYS

Although most of the work on phosphorus precipitation in silicon-germanium alloys reported by Ekstrom and Dismukes⁴ pertains to alloys with a silicon content of 70 a/o, they did extend it in a preliminary manner also to alloys with silicon contents of 80 a/o and 85 a/o. Most of this latter work, however, remains unreported. It has been necessary, therefore, to re-apply the theory to the 80 a/o Si - 20 a/o Ge and 63 a/o Si - 37 a/o Ge phosphorus doped alloys in an effort to determine the long-term behavior of their thermoelectric properties.

Underlying the present application of the precipitation model are experimental data on the time dependence of the electrical resistivity of phosphorus doped silicon-germanium alloys in the temperature range 400 to 800 °C for operating times up to 1500 hours. Some of these experimental data have been reported in Reference 1. The application of Eq. (2) to the experimental data has enabled the evaluation of constants in the equation. Maintaining the constants at fixed values, it has been possible to calculate the time dependence of the carrier concentration in the phosphorus doped silicon-germanium alloys. The carrier concentration values thus derived have been converted to electrical resistivity through the inclusion of electronic charge and carrier mobility, the dependence of the latter on carrier concentration being taken into account. Known relationships¹ between electrical resistivity and Seebeck coefficient for n-type

silicon-germanium alloys have been used to determine the time dependence of the Seebeck coefficient from the electrical resistivity data. The thermal conductivities of the alloys have been assumed to remain constant with time; experimental findings¹ give validity to this assumption for carrier concentration changes of several tens of percent. The effect of much greater changes in carrier concentration may, however, be observable and must be experimentally determined.

In critically evaluating the applicability of the above quantitative model to the precipitation of phosphorus in n-type silicon-germanium alloys it should be recognized that of all precipitation models this particular model probably best describes the observed time and temperature behavior of the thermoelectric properties. Even though this is the case, questions on the validity of the model naturally rise as a result of the fact that it does not accurately apply to very short precipitation times and the fact that its applicability to long time behavior is experimentally unverified. Probably the most disturbing aspect of the use of the model, as indeed is the case with nearly all precipitation models, is the need for knowledge of dopant solid solubility as a function of temperature. This information is generally not available for silicon-germanium alloys and must be estimated such that best agreement between theory and experiment obtains for time periods for which experimental data exist. Values for other adjustable constants must be similarly estimated. Probably the most serious criticism of the use of the model for predicting silicon-germanium alloy thermoelectric properties is the fact that because of the number of unknown variables in the model as used, the model does not necessarily lead to unique solutions. To obtain uniqueness, it has been necessary to assume temperature and time independence of some of these variables.

In view of the points raised in regards to the precipitation model, it will be realized that the long-term thermoelectric properties of silicon-germanium alloys derived by means of it are subject to some uncertainty; obviously, the longer

the time period over which projections are made, the greater is the uncertainty in derived thermoelectric properties. Nevertheless, it is believed that even at very long operating times, twelve years in the present instance, the uncertainty in the electrical resistivity values is no more than ± 5 to 10 percent. Because Seebeck coefficient values have been independently estimated on the basis of the electrical resistivity data, it is believed that even with the indicated uncertainty in electrical resistivity, the uncertainty in values of S^2 / ρ and figures-of-merit are considerably smaller, probably no more than a few percent. Inasmuch as S^2 / ρ and the figure-of-merit are directly proportional to the power output and conversion efficiency of a thermoelectric device, it is believed therefore that the presently derived thermoelectric property data enable a reasonably accurate accounting of device performance, even at very long operating times.

Although interest has recently developed in the use of silicon-germanium alloys, viz. the 80 a/o Si - 20 a/o Ge alloy, at operating temperatures higher than 1000°C , the present memorandum reports thermoelectric property data primarily to 1000°C because few experimental data have ever been obtained at higher temperatures. Some data for the 80 a/o Si - 20 a/o Ge alloy are given to 1200°C . Inasmuch as these data are based either on extrapolations and/or on a small number of measurements, it is suggested that care be used in their literal use. There are indications that the figure-of-merit of silicon-germanium alloys decreases at temperatures in excess of 1000°C because of a rapidly increasing thermal conductivity.

Figure 1 shows plots of electrical resistivity of the phosphorus doped 63 a/o Si - 37 a/o Ge alloy as a function of temperature for a variety of operating times in the range of zero hours to 12 years. It is to be recognized that the zero-hour data, the so-called initial data, are dependent on the details of crystal growth and related thermal history of the material and thus are not completely unique; samples with different thermal histories will have slightly different initial properties. Because slight changes in the electrical resistivity result in similar changes in the Seebeck coefficient, such that the quantity S^2 / ρ is nearly unchanged, the effect

of small differences in thermoelectric properties has little effect on device performance. Figure 2 shows the corresponding plots of the Seebeck coefficient, referenced to absolute. The thermal conductivity of the alloy is shown in Figure 3. Only one set of data is given for the thermal conductivity; as already mentioned above, for present purposes it has been assumed that the thermal conductivity of silicon-germanium alloys is independent of time. Figure 4 combines the data of Figures 1 to 3 into the figure-of-merit as a function of temperature and time. From Figure 4 it is seen that the biggest changes in the performance characteristics of the phosphorus doped 63 a/o Si - 37 a/o Ge alloy occur as a function of time in the temperature range of 300 to 600° C. It is also seen that the temperature of greatest change decreases with increasing operating time.

It should be noted that the electrical resistivity and Seebeck coefficient data given for the phosphorus doped 63 a/o Si - 37 a/o Ge alloy for the time period of zero hours to 1500 hours in Figures 1 and 2 are slightly different from those commonly attributed to the alloy. The reason for this is two-fold. First, the commonly used data are based on measurements of silicon-germanium alloys with silicon contents of about 61 a/o Si rather than 63 a/o Si. Second, the commonly used data are based on only five data points. The data in Figures 1 and 2 are based on more extensive and more recent measurements of an alloy that does have a silicon content of 63 a/o Si. The thermal conductivity data in Figure 3 are essentially the same as those determined for the 61 a/o Si - 39 a/o Ge alloy. The reason for this lies in the fact that the thermal conductivity of the silicon and germanium alloy system attains a relatively broad minimum in the silicon content range of 60 to 70 a/o Si. For alloy compositions in this range, the thermal conductivity is therefore nearly independent of composition.

The thermoelectric property data for the phosphorus doped 80 a/o Si - 20 a/o Ge alloy are shown as a function of time and temperature in Figures 5 to 8. Figure 5 shows plots of electrical resistivity as a function of temperature for a variety of operating times in the range of zero hours to 12 years. As with the data

for the 63 a/o Si - 37 a/o Ge alloy, it should be recognized that early life data are dependent on the past thermal history of the alloy and are thus subject to some variation from sample to sample. The effect of this variation on the performance characteristics of the alloy are generally minimal. Figure 6 shows plots of the Seebeck coefficient of the phosphorus doped 80 a/o Si - 20 a/o Ge alloy as a function of time and temperature. The thermal conductivity of the alloy is shown in Figure 7. Again as with the 63 a/o Si - 37 a/o Ge alloy, only one set of data is given for the thermal conductivity. Figure 8 combines the data of Figures 5 to 7 into the figure-of-merit as a function of temperature and time. It is seen that the biggest changes in the performance characteristics of the phosphorus doped 80 a/o Si 20 a/o Ge alloy take place in the temperature range of 350 to 600 °C.

It should be noted that inasmuch as the bulk of the experimental data underlying the calculated long-term electrical properties of phosphorus doped silicon-germanium alloys shown in Figures 1, 2, 5 and 6 pertain to temperatures of 400 °C and higher, there is some question as to the precise temperature dependence of these properties at lower temperatures. The property curves for times exceeding the initial time have been estimated on the basis that at very low temperatures, between room temperature and 100 to 200 °C, the thermoelectric properties of silicon-germanium alloys undergo practically no change with time. The electrical properties between 100 to 200 °C and 400 °C are thus the results of interpolation; any uncertainty in these properties has little effect on the calculated performance of devices that operate over extended temperature ranges.

As indicated in the Introduction, the present work primarily pertains to the thermoelectric properties of phosphorus doped n-type silicon-germanium alloys. Although changes have been observed in the thermoelectric properties of boron doped p-type silicon-germanium alloys, these changes are significantly smaller than those in the n-type alloys and little experimental basis exists at present for long-term

predictions of these changes. It is believed therefore that beginning-of-life thermoelectric data can be used for the boron doped p-type silicon-germanium alloys even at long operating times without undue error. For completeness, such data for the 63 a/o Si - 37 a/o Ge and 80 a/o Si - 20 a/o Ge alloys are given in Figures 9 to 12. Figure 9 shows the electrical resistivities of these alloys as a function of temperature. The corresponding Seebeck coefficient and thermal conductivity data are plotted in Figures 10 and 11. Figure 12 combines the data of Figures 9 to 11 into the figures-of-merit of the two alloys.

The thermoelectric property data for the boron doped p-type silicon-germanium alloys in Figures 9 to 12 pertain to specific levels of boron doping. It should be realized that doping variations, either purposely incorporated or due to process fluctuations, usually exist between different lots of any given material. As long as these variations are relatively minor, of the order of 20 to 30 percent or less, the effect of doping variations on the figure-of-merit and consequently on the performance obtainable with silicon-germanium alloys is nearly negligible. Changes in the electrical resistivity and the Seebeck coefficient are nearly self-compensating such that the quantity S^2 / ρ is practically independent of small doping variations; the thermal conductivity is similarly nearly unaffected.

Although the bulk of the thermoelectric property data underlying the present memorandum are those measured for melt grown (zone levelled) silicon-germanium alloys, it is believed that they equally pertain to hot pressed and even vacuum cast alloys. Unlike with some other semiconductor materials, the thermoelectric properties of silicon-germanium alloys are practically independent of the method of preparation. While it remains to experimentally confirm that the long-time behavior of these properties is also independent of material preparation method, there is no special reason at this time for it to be questioned.

The thermal conductivity data of the 63 a/o Si - 37 a/o Ge alloy, both n - and p - type, presented in this memorandum have been obtained from measured values of thermal diffusivity and calculated values of specific heat.¹ The specific heat values used are those calculated by Steigmeier and Kudman⁶ and later experimentally confirmed by Gerlich, Abeles and Miller.⁷ A question⁸ has subsequently arisen on the experimental technique used by the latter investigators. Even though recent specific heat measurements have been performed on the 80 a/o Si - 20 a/o Ge alloy at Sandia Laboratories and the Battelle Memorial Institute, this question has not been conclusively settled to date because of limited experimental results. Although the specific heat of a number of n - and p - type samples were measured at Sandia, the measurements spanned only the temperature range of room temperature to about 500°C. The specific heat measurements performed at Battelle covered the whole range of temperatures from room temperature to 1200°C, but only involved one p - type 80 a/o Si - 20 a/o Ge alloy sample. On the basis of the latter measurements it was found that the calculated specific heat values of Steigmeier and Kudman are generally higher, except in the temperature range of about 200 to 600°C, than those measured. The biggest discrepancy between measured and calculated specific heat values occurs at high temperatures and is of the order of five percent. It is not known whether a similar discrepancy between measured and calculated specific heat values also exists in the case of the 63 a/o Si - 37 a/o Ge alloy and, moreover, whether n - and p - type silicon - germanium alloys have measurably different values of specific heat. Although uncertainties thus exist in the calculated values of specific heat of silicon - germanium alloys, for lack of experimental data, it has been deemed advisable for the purposes of the present memorandum to retain the use of calculated values of specific heat for the 63 a/o Si - 37 a/o Ge alloy even though it is recognized that the calculated values may well be somewhat in error.

The thermal conductivity data of the n - and p - type 80 a/o Si - 20 a/o Ge alloy in Figures 7 and 11 are average data based on a fairly large number of samples independently measured at several laboratories. These data, although also derived from thermal diffusivity measurements, at least approximately account for uncertainties in calculated specific heat values and thus should be fairly accurate. It should be noted that the thermoelectric property data given in this memorandum for the n - and p - type 80 a/o Si - 20 a/o Ge alloy are data mutually agreed upon by a number of groups interested in this alloy* and will be used by these groups until additional information warrants the updating of the data. The thermoelectric property data given in this memorandum for the n - and p - type 63 a/o Si - 37 a/o Ge alloy are data based on less extensive experimentation and have not undergone as much evaluation as those of the higher silicon content alloy. Nevertheless, it is believed that these data are reasonably accurate. The area of greatest question, that of specific heat values, should however be experimentally further explored for the 63 a/o Si - 37 a/o Ge alloy. The available information on the specific heats of 63 a/o Si - 37 a/o Ge and 80 a/o Si - 20 a/o Ge alloys is summarized in Figure 13 in terms of plots as a function of temperature. Figure 13 shows the calculated specific heats of the two silicon - germanium alloys, along with the experimental values obtained at the Battelle Memorial Institute for the 80 a/o Si - 20 a/o Ge alloy. Although originally reported in terms of per unit mass, for sake of consistency, the latter values are here given in terms of specific heat per unit volume. Volume expansion with temperature has been taken into account.

The thermoelectric property data depicted in Figures 1 to 12 are tabularized for convenience in Tables I to IV. Tables I and II give the thermoelectric property data of the n - and p - type 63 a/o Si - 37 a/o Ge alloy, respectively whereas Tables III and IV give the corresponding data for the n - and p - type 80 a/o Si - 20 a/o Ge alloy.

* Meeting between representatives of JPL, Resalab, AEC, Sandia, GE and RCA, Harrison, New Jersey, on August 19, 1970.

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TABLE I

THERMOELECTRIC PROPERTIES OF PHOSPHORUS DOPED

63 a/o Si - 37 a/o Ge ALLOY

TEMP. °C	ELECTRICAL RESISTIVITY m Ω - cm					SEEBECK COEFFICIENT * μ v / ° C					THERMAL COND. Watts/°C -cm
	Initial	1500 Hrs.	1 Year	5 Years	12 Years	Initial	1500 Hrs.	1 Year	5 Years	12 Years	
0	1.42	1.42	1.42	1.42	1.42	150	150	150	150	150	0.0525
100	1.63	1.68	1.68	1.68	1.68	186	186	186	186	186	0.0484
200	2.03	2.12	2.24	2.38	2.65	222	226	233	238	250	0.0448
300	2.44	3.40	4.12	5.75	8.04	251	282	306	341	375	0.0418
400	2.90	4.93	6.06	6.83	7.16	276	332	353	369	374	0.0393
500	3.28	4.83	5.33	5.75	6.02	295	335	345	352	357	0.0375
600	3.10	4.09	4.47	4.75	4.96	294	322	331	337	342	0.0366
700	2.61	3.34	3.65	3.83	3.98	282	301	313	320	323	0.0368
800	2.21	2.66	2.88	3.02	3.13	271	286	295	299	303	0.0385
900	1.95	2.19	2.30	2.40	2.47	264	274	278	282	284	0.0416
1000	1.75	1.82	1.87	1.91	1.93	260	264	266	267	268	0.0456

* Referenced to Absolute

TABLE II
THERMOELECTRIC PROPERTIES OF BORON DOPED
63 a/o Si - 37 a/o Ge ALLOY

TEMP. ° C	ELECTRICAL RESISTIVITY m Ω- cm	SEEBECK COEFFICIENT μ v / ° C	THERMAL CONDUCTIVITY Watts / ° C - cm
0	0.94	109	0.0590
100	1.06	130	0.0562
200	1.20	154	0.0537
300	1.37	175	0.0512
400	1.55	195	0.0490
500	1.75	213	0.0470
600	1.96	230	0.0454
700	2.17	246	0.0442
800	2.40	260	0.0436
900	2.62	272	0.0451
1000	2.87	284	0.0515

* Referenced to Absolute

TABLE III
THERMOELECTRIC PROPERTIES OF PHOSPHORUS DOPED
80 a/o Si - 20 a/o Ge ALLOY

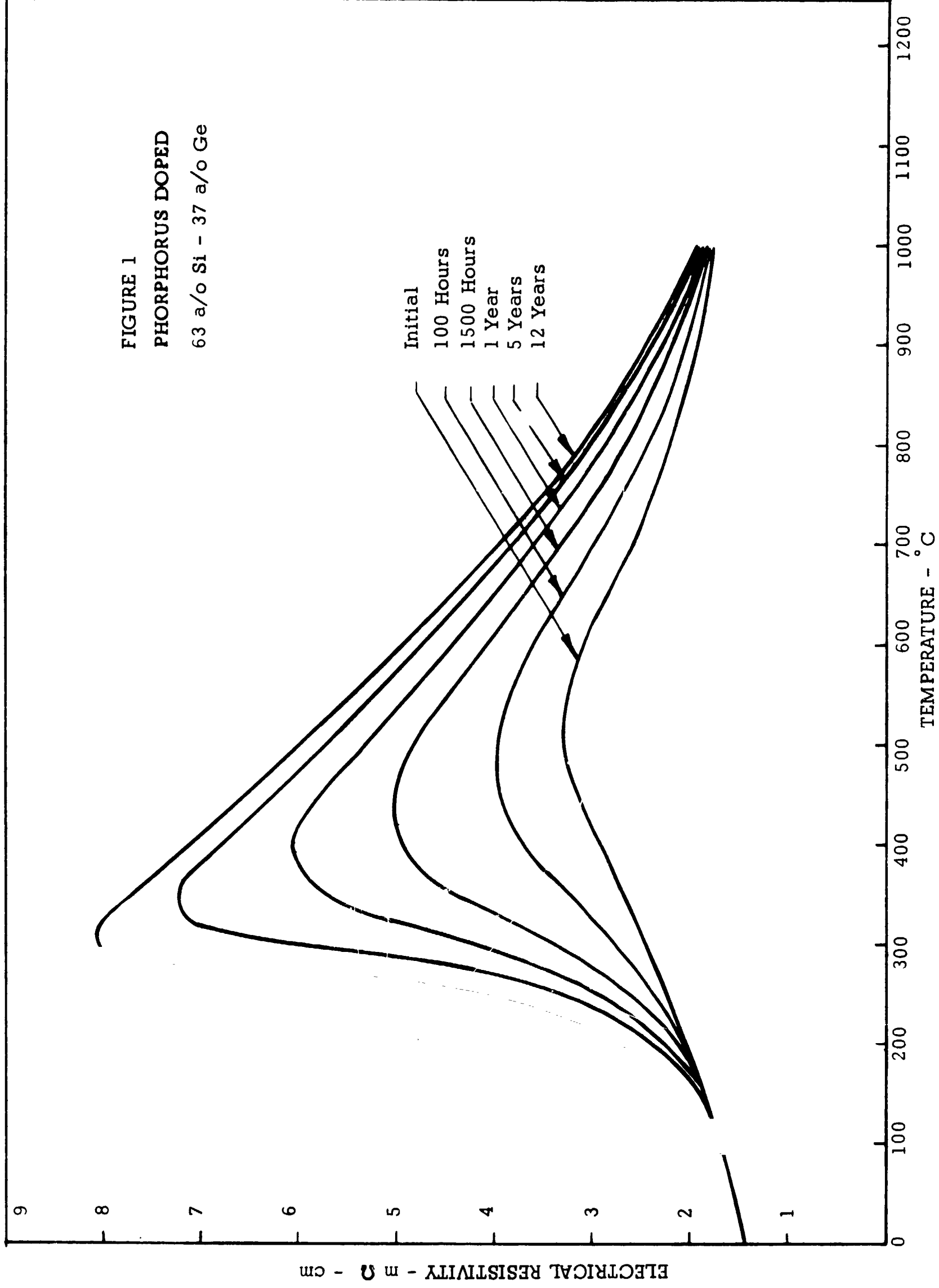
TEMP. ° C	ELECTRICAL RESISTIVITY m Ω - cm					SEEBECK COEFFICIENT * μ v / ° C					THERMAL COND. Watts/ ° C - cm
	Initial	1500 Hrs	1 Year	5 Years	12 Years	Initial	1500 Hrs.	1 Year	5 Years	12 Years	
0	0.90	0.90	0.90	0.90	0.90	113	113	113	113	113	0.0514
100	1.08	1.08	1.08	1.08	1.08	145	145	145	145	145	0.0490
200	1.29	1.35	1.45	1.59	1.74	176	181	187	196	206	0.0468
300	1.51	1.98	2.30	2.80	3.30	204	229	245	265	282	0.0447
400	1.75	2.99	3.74	4.50	4.90	228	279	302	322	330	0.0431
500	1.97	3.25	3.63	4.00	4.21	246	294	305	315	320	0.0418
600	2.04	2.79	3.10	3.35	3.54	254	284	294	302	307	0.0412
700	1.88	2.28	2.54	2.75	2.91	252	269	279	287	292	0.0412
800	1.61	1.84	2.03	2.21	2.32	246	256	264	271	275	0.0423
900	1.40	1.49	1.61	1.73	1.81	242	246	251	256	258	0.0447
1000	1.22	1.26	1.30	1.34	1.37	239	240	242	244	245	0.0483
(1100)	-	(1.09)	-	-	-	-	(235)	-	-	-	(0.0538)
(1200)	-	(1.00)	-	-	-	-	(231)	-	-	-	(0.0623)

* Referenced to Absolute

TABLE IV
THERMOELECTRIC PROPERTIES OF BORON DOPED
80 a/o Si - 20 a/o Ge Alloy

TEMP. ° C	ELECTRICAL RESISTIVITY m Ω - cm	SEEBECK COEFFICIENT * μ v / ° C	THERMAL CONDUCTIVITY Watts / ° C - cm
0	0.97	122	0.0584
100	1.08	145	0.0563
200	1.21	166	0.0541
300	1.38	185	0.0517
400	1.61	204	0.0499
500	1.83	222	0.0472
600	2.05	238	0.0468
700	2.27	254	0.0460
800	2.49	269	0.0458
900	2.71	283	0.0466
1000	2.92	298	0.0497
(1100)	(3.13)	(313)	(0.0553)
(1200)	(3.33)	(328)	(0.0640)

* Referenced to Absolute



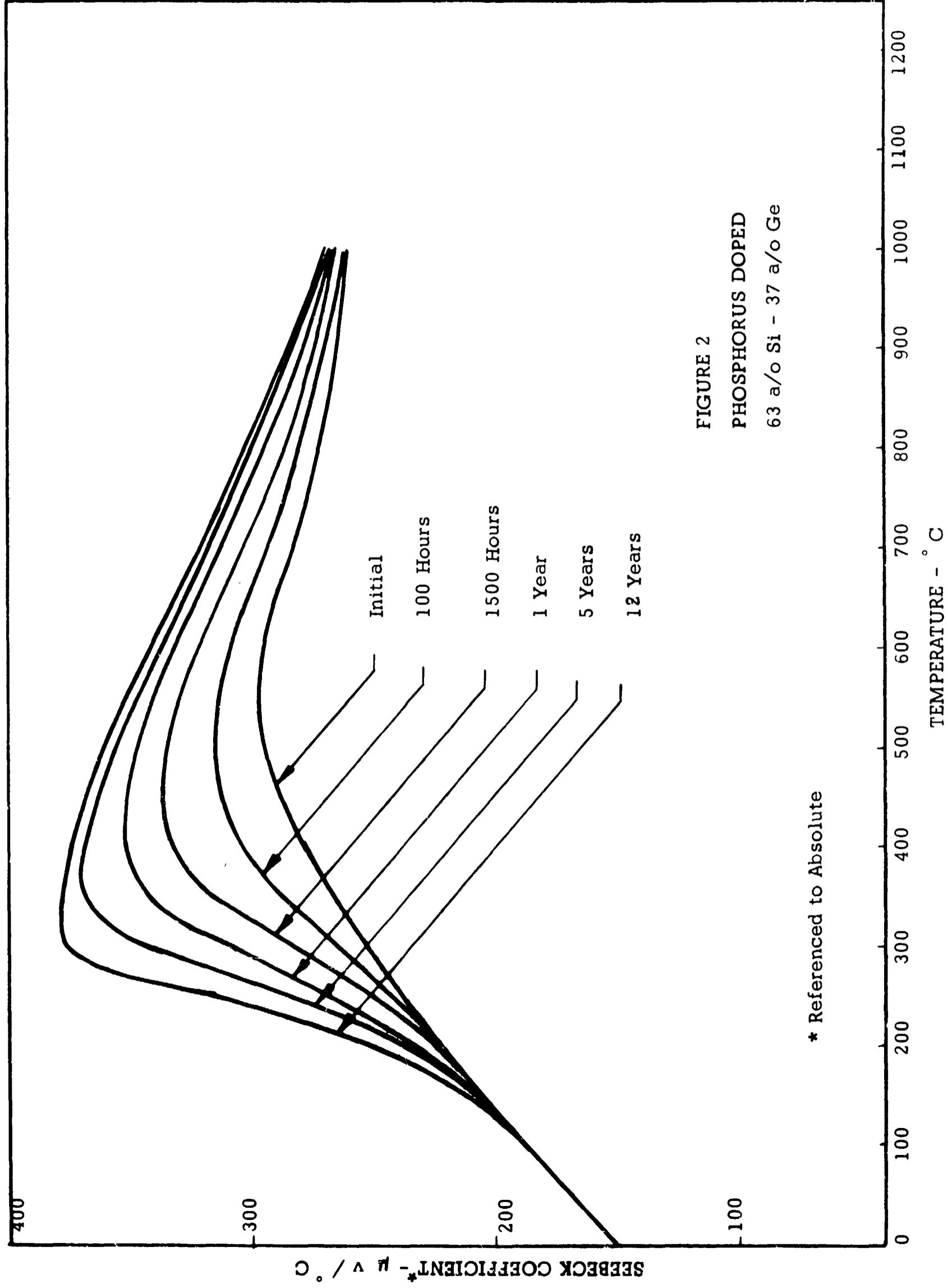
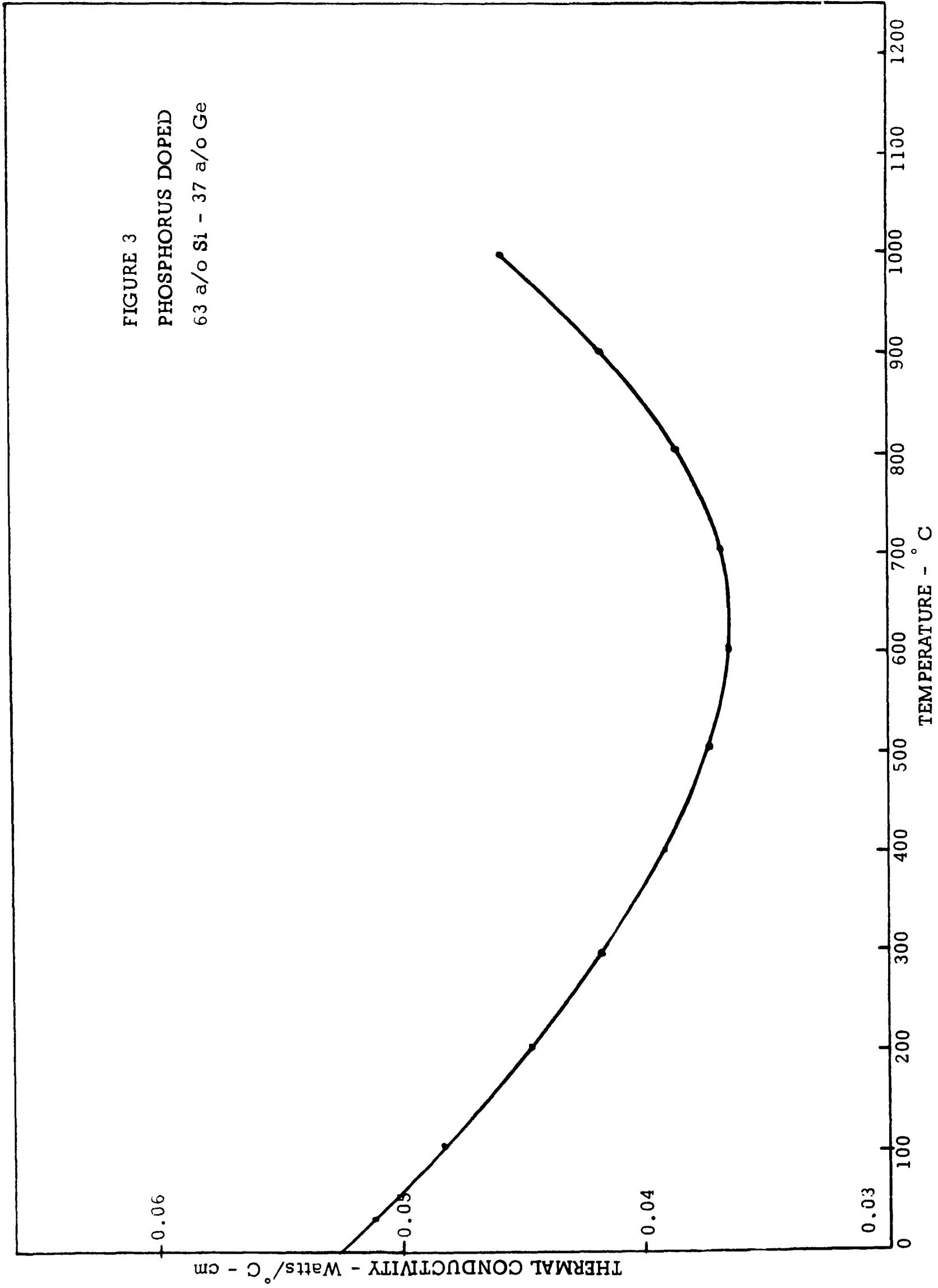


FIGURE 2
PHOSPHORUS DOPED
63 a/o Si - 37 a/o Ge

FIGURE 3
PHOSPHORUS DOPED
63 a/o Si - 37 a/o Ge



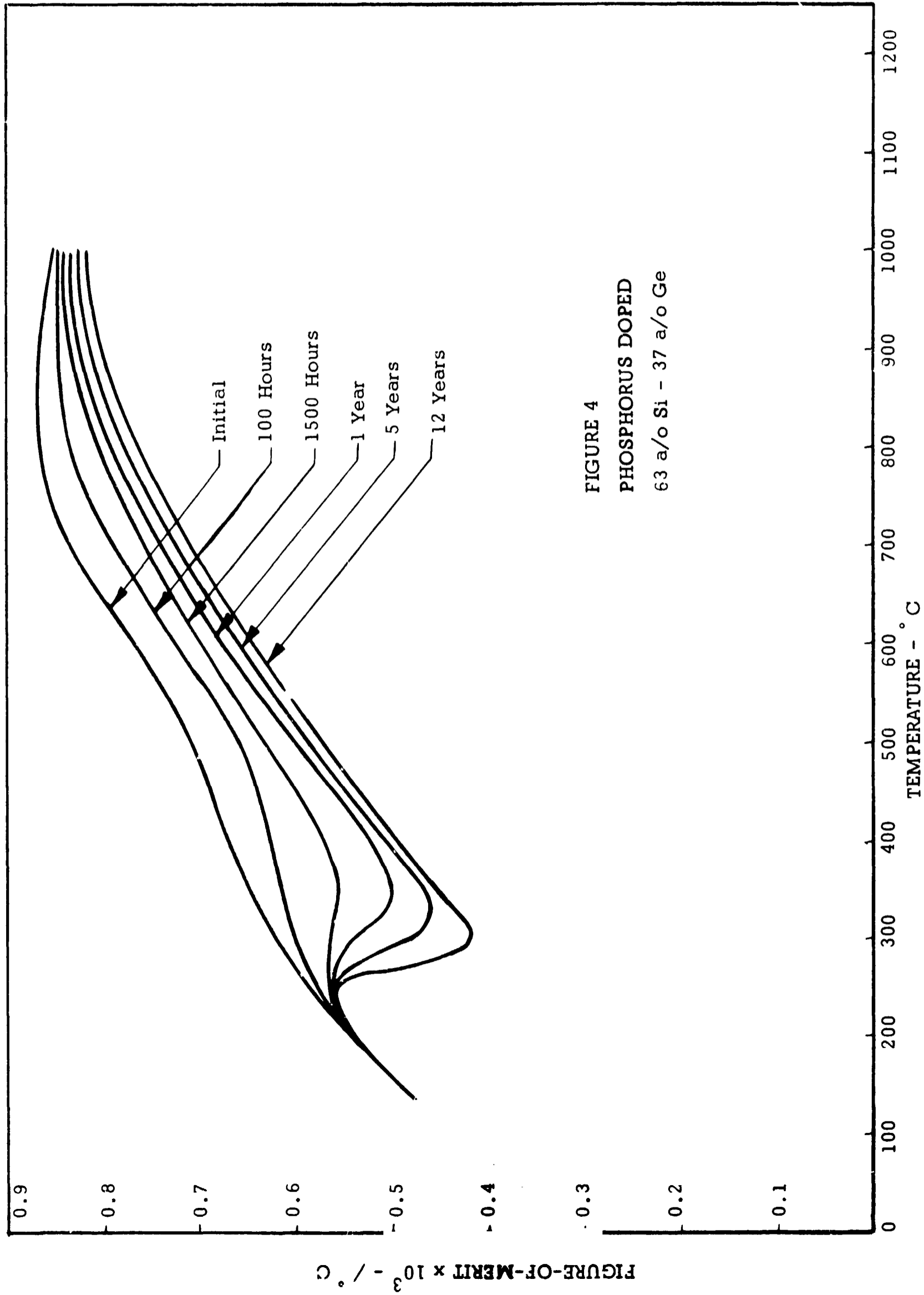
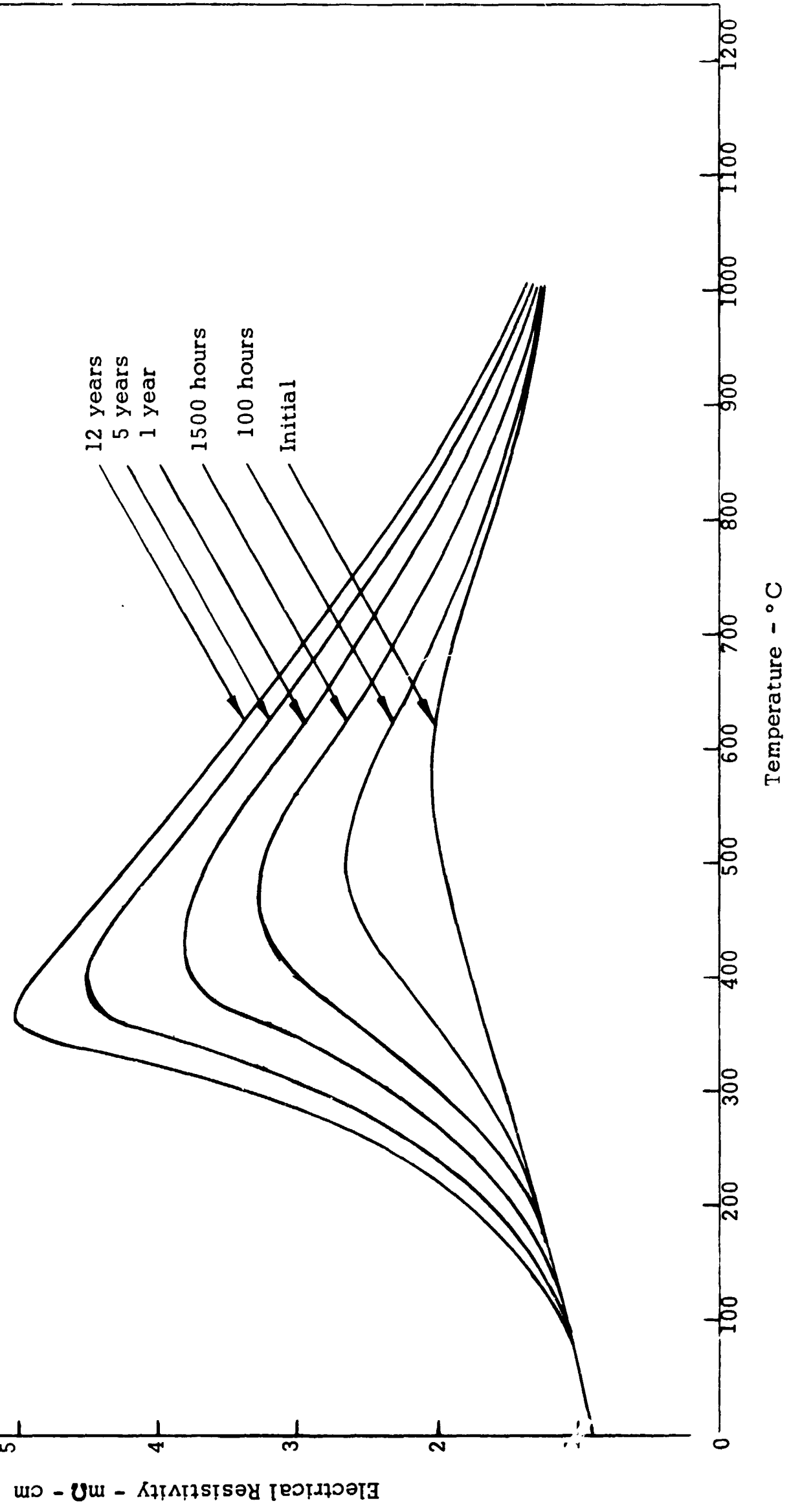


FIGURE 4
PHOSPHORUS DOPED
63 a/o Si - 37 a/o Ge

Figure 5
Phosphorus Doped
80 a/o Si - 20 a/o Ge



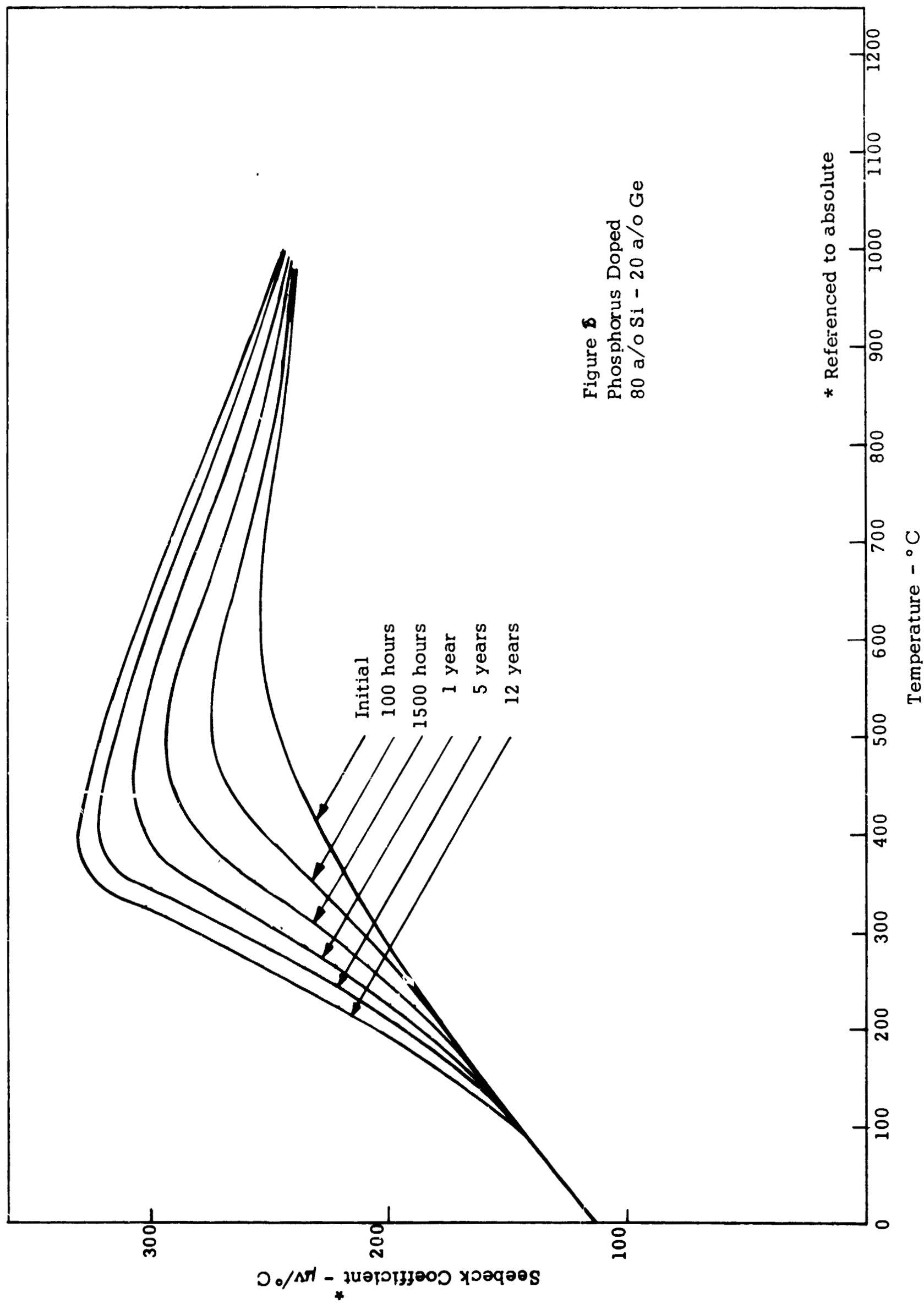
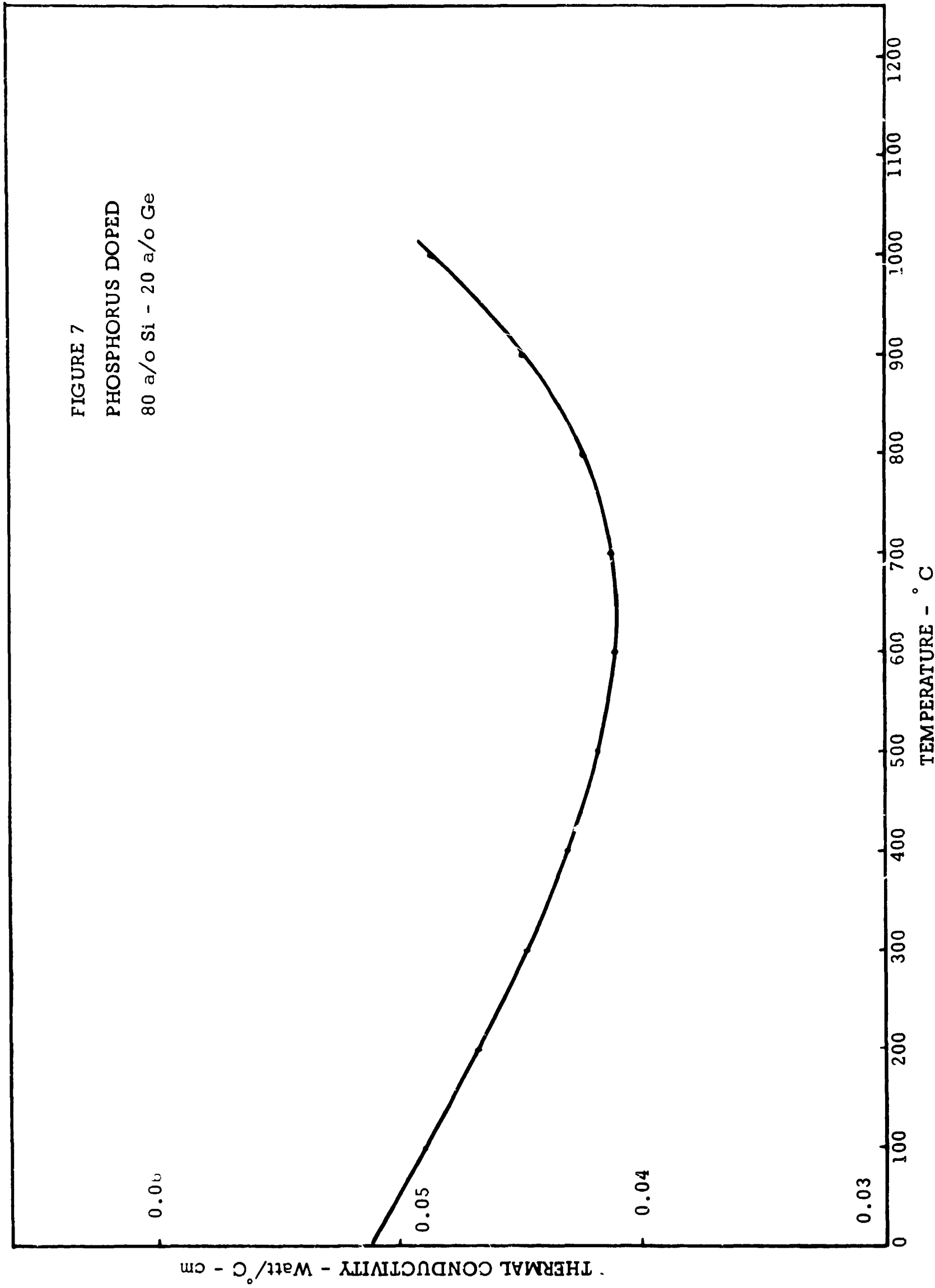
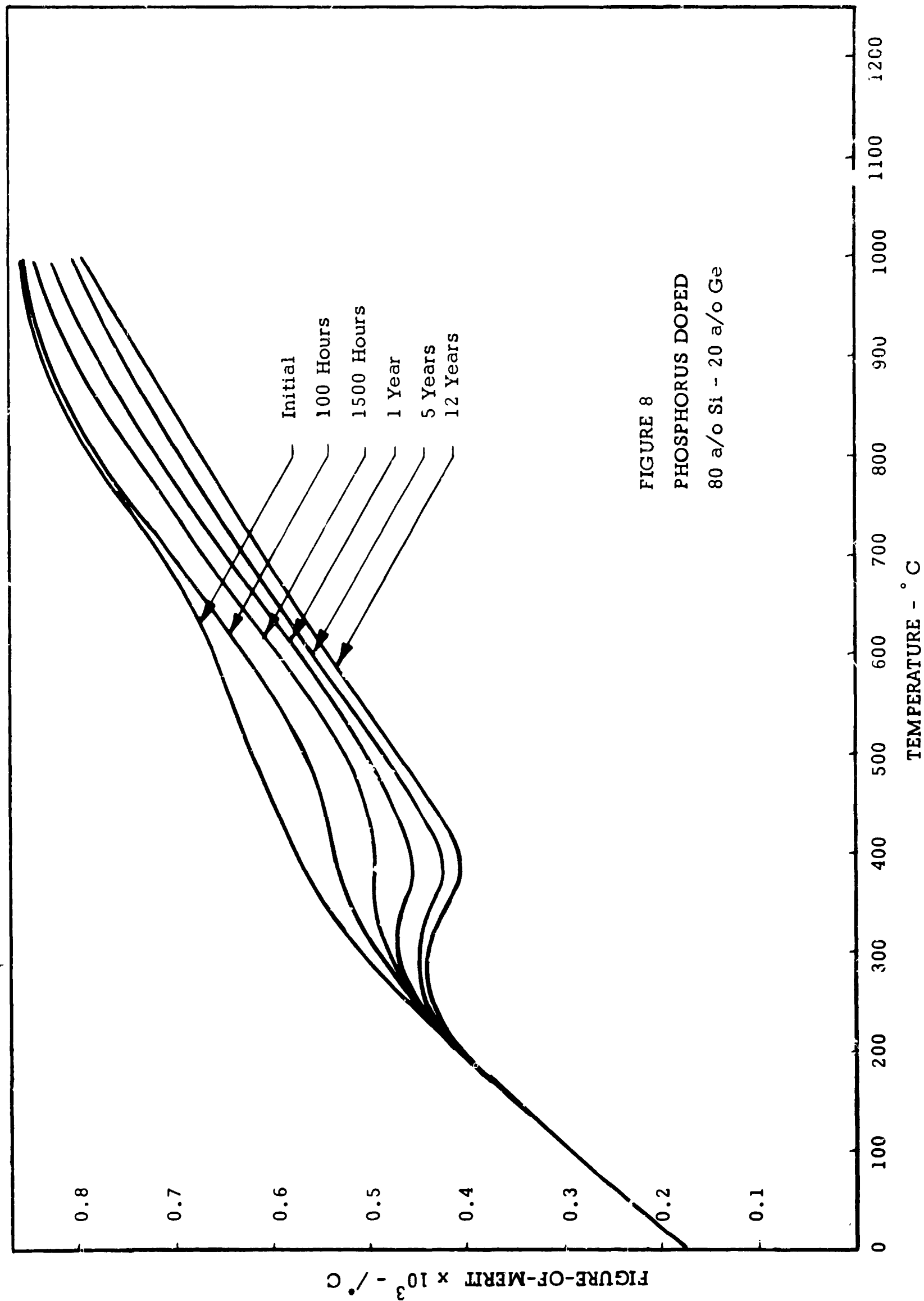


Figure 8
Phosphorus Doped
80 a/o Si - 20 a/o Ge

* Referenced to absolute





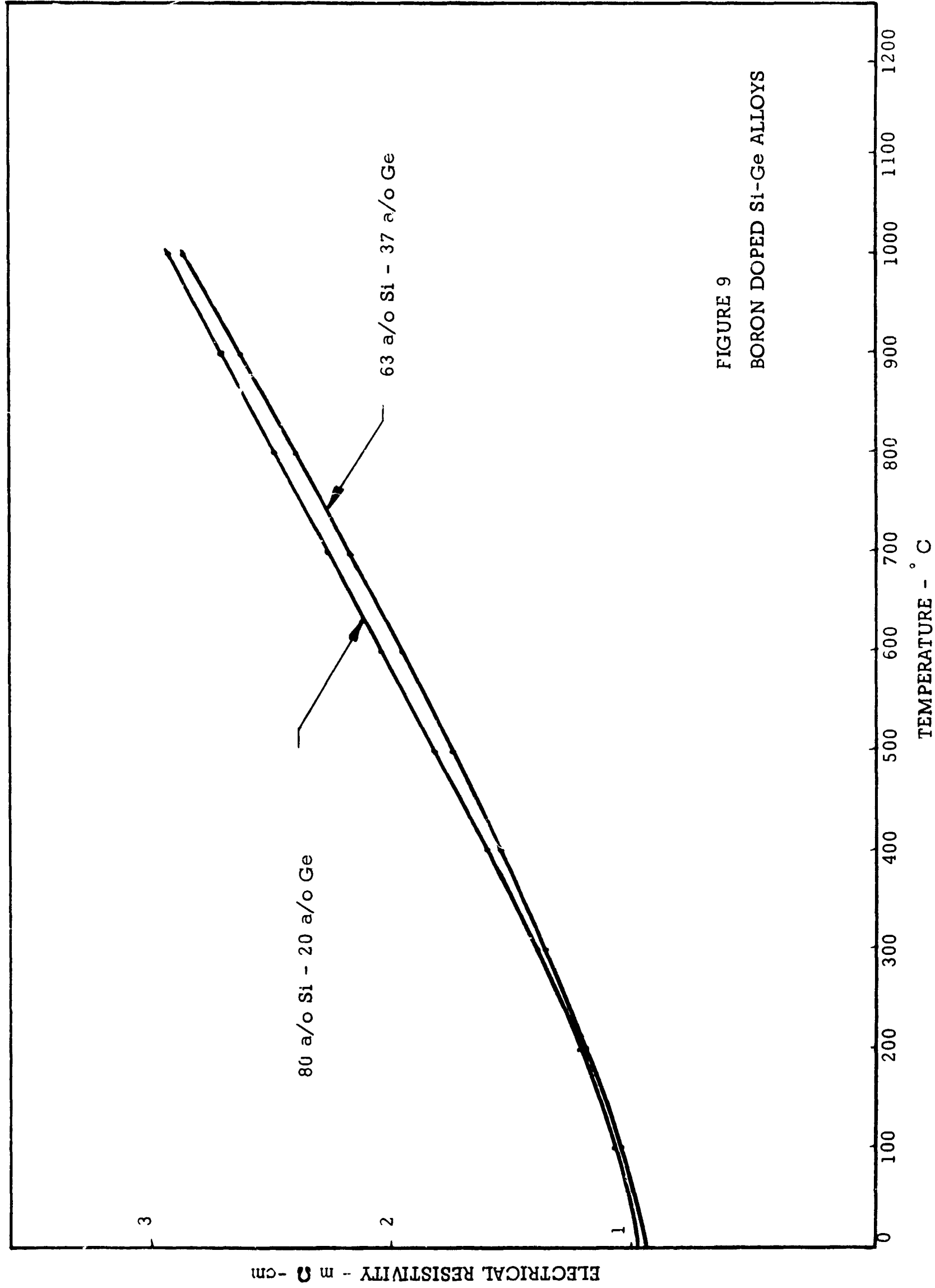


FIGURE 9
BORON DOPED Si-Ge ALLOYS

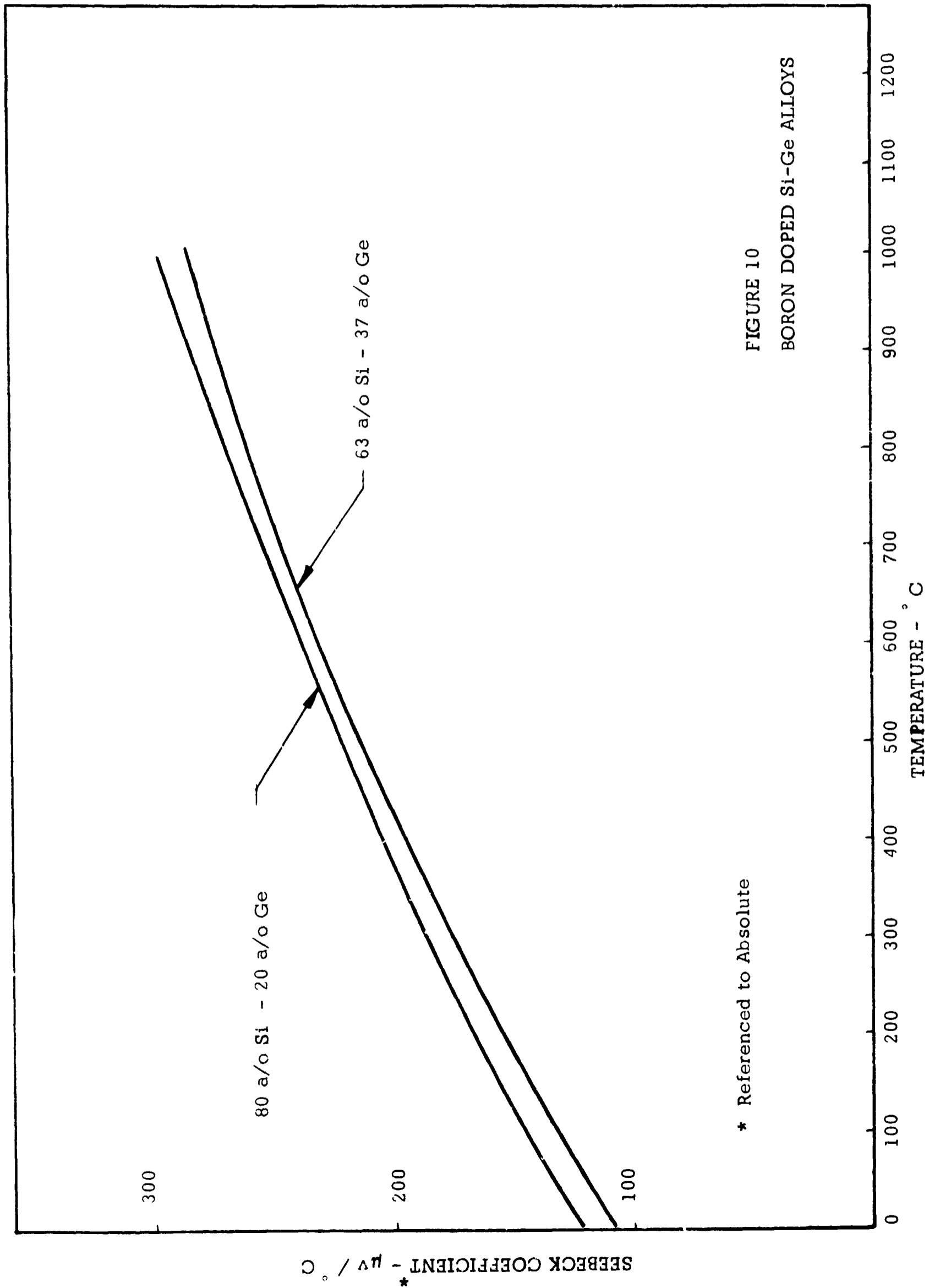


FIGURE 10
BORON DOPED Si-Ge ALLOYS

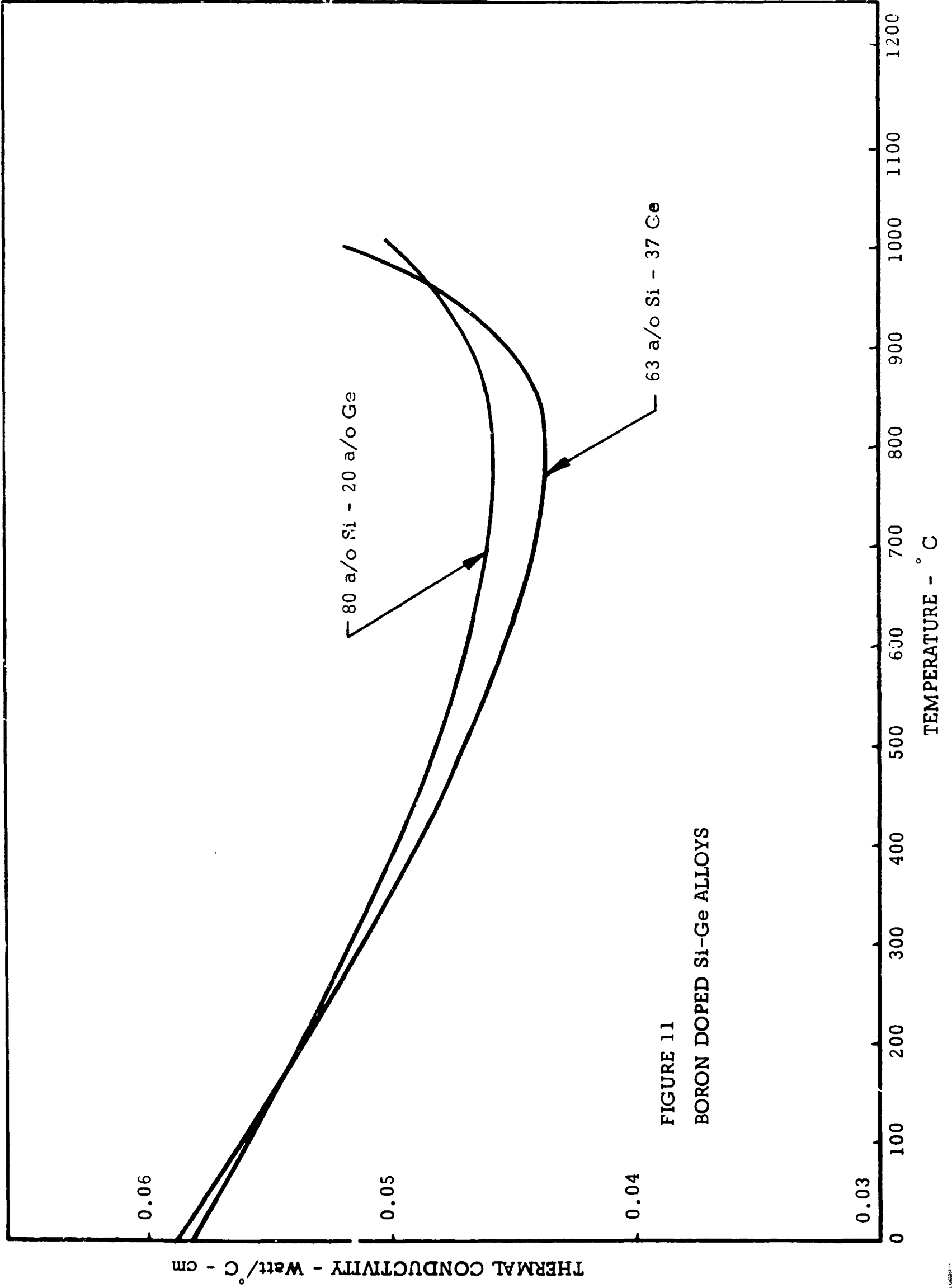


FIGURE 11
BORON DOPED Si-Ge ALLOYS

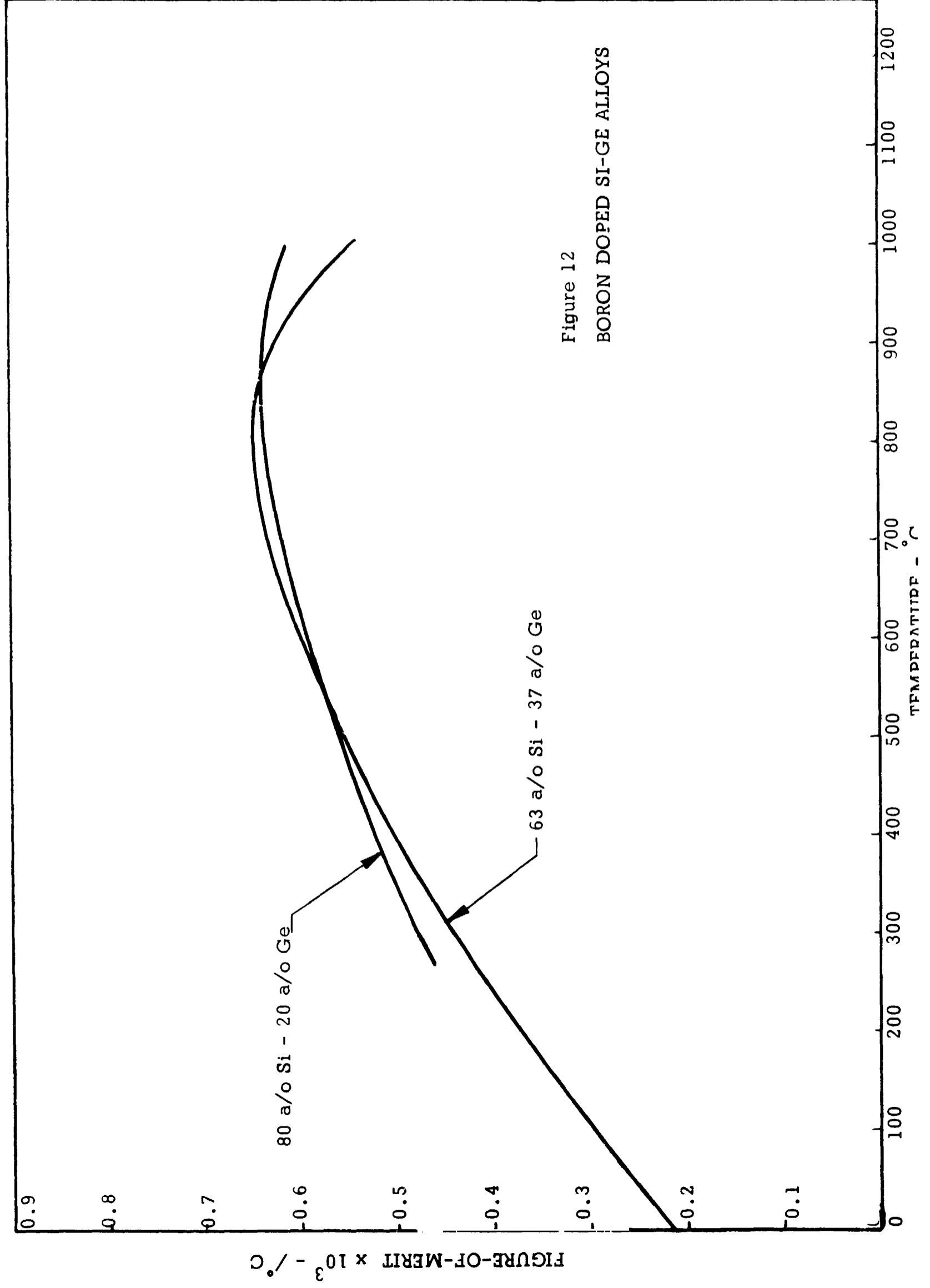


Figure 12
BORON DOPED SI-GE ALLOYS

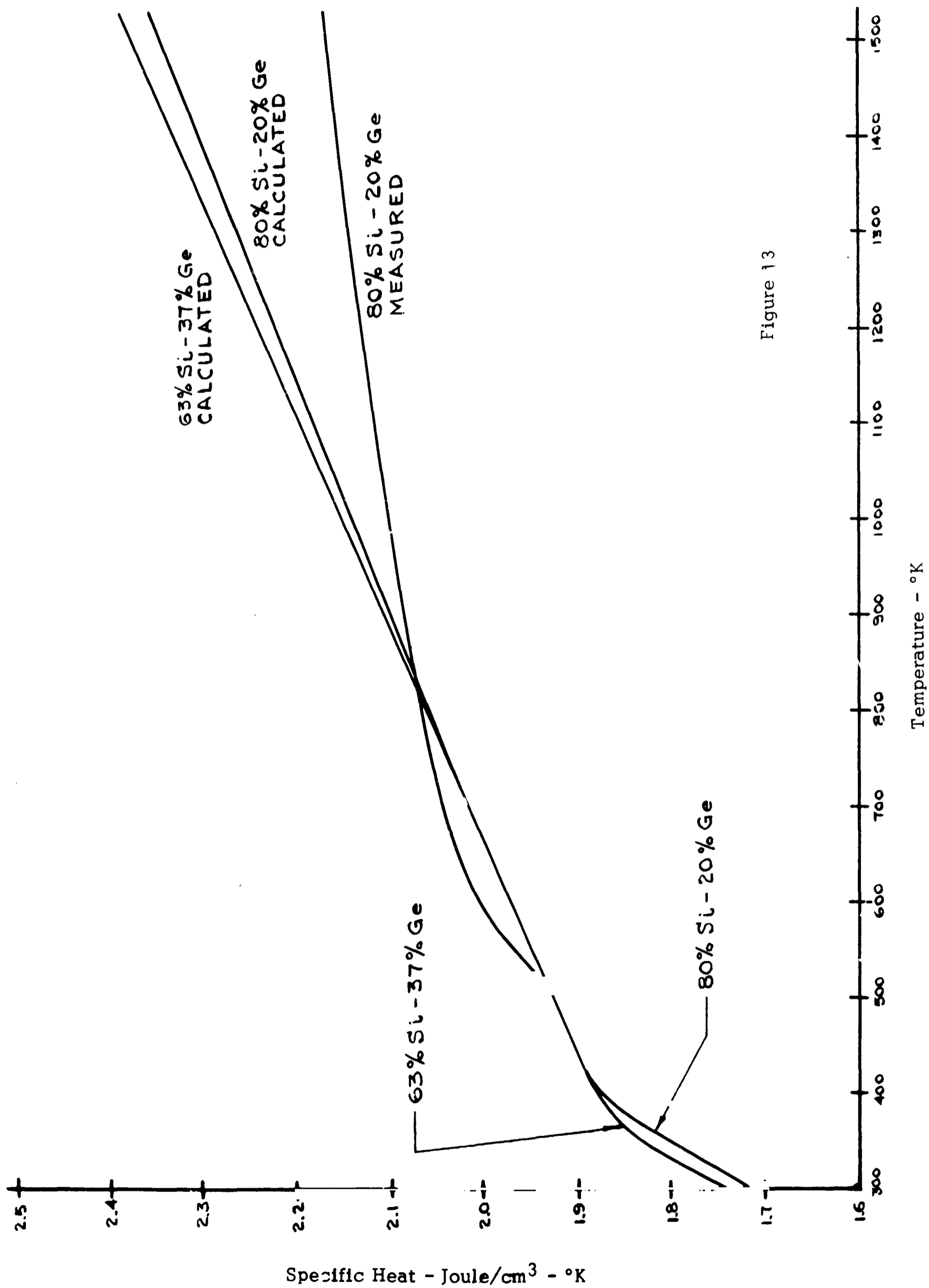


Figure 13